

AD-A278 940

PORT DOCUMENTATION PAGE

2

2. REPORT DATE
April 8, 19943. REPORT TYPE AND DATES COVERED
Final Report, Feb. 1, 1992 through Jan. 30, 1994

4. TITLE AND SUBTITLE Vacuum Ultraviolet Studies of Molecular Dynamics		5. FUNDING NUMBERS 611102F 2303 ES	
6. AUTHOR(S) Paul L. Houston			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Cornell University 120 Day Hall Ithaca, NY 14853-2801		8. PERFORMING ORGANIZATION REPORT NUMBER AFOSR-TR- 94 0277	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NC Bldg 410, Bolling AFB DC 20332-6448		10. SPONSORING/MONITORING AGENCY REPORT NUMBER F49620-92-J-0080	
11. SUPPLEMENTARY NOTES The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.			
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.		12b. DISTRIBUTION CODE	
13. ABSTRACT (maximum 200 words) Tunable vacuum ultraviolet radiation generated by four-wave mixing will be used to probe collisional energy transfer and photodissociation. Collisional relaxation of the S(¹ D) velocity distribution by rare gases has been measured to learn to what extent this simple process can be described by a hard-sphere, elastic interaction. E→V transfer was studied from S(¹ D) to CO and N ₂ , both by examining the Doppler profile of the relaxed atoms and by direct measurement of the CO(v,J) distribution. Finally, the photodissociation of O ₃ and N ₂ O have been investigated by monitoring the Doppler profiles of the resulting O(¹ D) lines. This integrated program of molecular dynamics studies using vacuum ultraviolet radiation has enhanced our knowledge both of the chemical physics of these basic processes and of the interaction of high energy photons with small molecules found in the upper atmosphere.			
14. SUBJECT TERMS Vacuum Ultraviolet Light, Molecular Dynamics, Ozone, Nitrous Oxide, CO		15. NUMBER OF PAGES 7	
		16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UNCLASSIFIED

DDFORM 1473, 84 Mar

Unclassified

94-13601



108

94 5 05 087

TITLE: Vacuum Ultraviolet Studies of Molecular Dynamics

PRINCIPAL INVESTIGATOR: Paul L. Houston

Approved for public release;
distribution unlimited.

CONTRACT/GRANT NUMBER: F49620-92-J-0080

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PUBLICATIONS:

1. G. C. McBane, I. Burak, G. E. Hall, and P. L. Houston, "The $S(^1D) + N_2$ Quenching Process: Determination of the Branching Ratio among Triplet Fine Structure Products," *J. Phys. Chem.* **96**, 753-755 (1992).
2. R. L. Miller, S. H. Kable, P. L. Houston, and I. Burak, "Product Distributions in the 157-nm Photodissociation of CO_2 ," *J. Chem. Phys.* **96**, 332-338 (1992).
3. G. Nan and P. L. Houston, "Velocity Relaxation of $S(^1D)$ by Rare Gases Measured by Doppler Spectroscopy," *J. Chem. Phys.* **97**, 7865-7872 (1992).
4. G. Nan, D. W. Neyer, P. L. Houston, and I. Burak, "Electronic-to-vibrational, -Rotational, and -Translational Energy Transfer: $S(^1D) + CO, N_2, O_2$ and CO_2 Measured by Doppler Spectroscopy," *J. Chem. Phys.* **98**, 4603-4609 (1993).
5. L. L. Springsteen, S. Satyapal, Y. Matsumi, L. M. Dobeck, and P. L. Houston, "Anisotropy and Energy Disposal in the 193-nm N_2O Photodissociation measured By VUV Laser-Induced Fluorescence of $O(^1D)$," *J. Chem. Phys.* **97**, 7239-7241 (1993).
6. G. Nan, I. Burak, and P. L. Houston, "Photodissociation of OCS at 222 nm: The Triplet Channel," *Chem. Phys. Lett.* **209**, 383 (1993).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Tunable vacuum ultraviolet radiation generated by four-wave mixing will be used to probe collisional energy transfer and photodissociation. Collisional relaxation of the $S(^1D)$ velocity distribution by rare gases has been measured to learn to what extent this simple process can be described by a hard-sphere, elastic interaction. $E \rightarrow V$ transfer was studied from $S(^1D)$ to CO and N_2 , both by examining the Doppler profile of the relaxed atoms and by direct measurement of the $CO(v,J)$ distribution. Finally, the photodissociation of O_3 and N_2O have been investigated by monitoring the Doppler profiles of the resulting $O(^1D)$ lines. This integrated program of molecular dynamics studies using vacuum ultraviolet radiation has enhanced our knowledge both of the chemical physics of these basic processes and of the interaction of high energy photons with small molecules found in the upper atmosphere.

Final Technical Report**F49620-92-J-0080****April 8, 1994****Vacuum Ultraviolet Studies of Molecular Dynamics**

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Abstract

Tunable vacuum ultraviolet radiation generated by four-wave mixing will be used to probe collisional energy transfer and photodissociation. Collisional relaxation of the $S(^1D)$ velocity distribution by rare gases has been measured to learn to what extent this simple process can be described by a hard-sphere, elastic interaction. $E \rightarrow V$ transfer was studied from $S(^1D)$ to CO and N_2 , both by examining the Doppler profile of the relaxed atoms and by direct measurement of the $CO(v,J)$ distribution. Finally, the photodissociation of O_3 and N_2O have been investigated by monitoring the Doppler profiles of the resulting $O(^1D)$ lines. This integrated program of molecular dynamics studies using vacuum ultraviolet radiation has enhanced our knowledge both of the chemical physics of these basic processes and of the interaction of high energy photons with small molecules found in the upper atmosphere.

A. Summary of Completed Work (Projects in 1992 and 1993 with AROSR Support)

1. The $S(^1D) + N_2$ Quenching Process: Determination of the Branching Ratio among Triplet Fine Structure Products

The quenching by N_2 of $S(^1D)$ to the $S(^3P_2)$, $S(^3P_1)$, and $S(^3P_0)$ levels has been investigated by using tunable vacuum ultraviolet laser-induced fluorescence to probe the initial and final levels following creation of $S(^1D)$ by pulsed 222-nm photolysis of OCS. The total quenching rate is $(7.1 \pm 1.0) \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$, while the branching ratios were found to be $0.143 \pm .006$ for 3P_0 , $0.085 \pm .012$ for 3P_1 , and $0.77 \pm .02$ for 3P_2 . The total rate is in good agreement with previous measurements. The branching ratios contrast to the inverted distribution found by Stout, Andrews, Bevilacqua, and Weisman for quenching of $S(^1D)$ by argon [*Chem. Phys. Lett.* 1988, 151, 156].

2. Product Distributions in the 157-nm Photodissociation of CO₂

The vibrational and rotational distributions of CO ($^1\Sigma_g^+$) produced in the 157 nm photodissociation of CO₂ have been determined by measuring vacuum-ultraviolet laser-induced fluorescence spectra of the CO photoproduct. The photodissociation of CO₂ is known to occur via two pathways; one yielding O(1D) and the other yielding O(3P). Spin conservation and previous experimental studies confirm that dissociation via the O(1D) channel is the dominant process. The available energy for this channel is sufficient to populate only the ground and first excited vibrational levels of CO. We measured the rotational distributions for CO in $v=0$ and $v=1$ and found them to be non-Boltzmann. In fact, a highly structured distribution with distinct peaks at $J=10, 24, 32$ and 39 is observed for CO in $v=0$. A less structured population is displayed by molecules in $v=1$. The relative vibrational population ($v=0/v=1$) was determined to be 3.7 ± 1.2 . Doppler spectra of individual rovibronic transitions were also recorded. The profiles have widths in accord with the available translational energy, display the expected $v \perp J$ correlation, and are best described by an isotropic distribution of the velocity vectors with respect to the polarization direction of the dissociation light.

3. Velocity Relaxation of S(1D) by Rare Gases Measured by Doppler Spectroscopy

Velocity relaxation of S(1D) by He, Ar, and Xe has been monitored by measuring the Doppler profile of the S(1D) for variable collision partner pressures at a fixed time delay following creation of S(1D) by pulsed laser photolysis of OCS at 222 nm. The nascent S(1D) has a mean speed about three times that at room temperature and an effective anisotropy parameter of $\beta=0.5$. A calculation assuming elastic hard-sphere collisions is performed to model the process. The data are in qualitative agreement with the model in that the angular distribution relaxes more rapidly with collision number as the mass

ratio between the collision partner and sulfur approaches infinity, whereas the speed distribution relaxes more rapidly as the mass ratio approaches zero. Helium behaves as predicted by the hard-sphere model with a collision cross section of $\sigma_{\text{col}} = 26 \pm 2 \text{ \AA}^2$. However, the cross sections for argon and xenon are found to depend on the collision energy. The dependence allows an estimation of the following Lennard-Jones parameters: for argon $\sigma = 3.6 \pm 0.5 \text{ \AA}$ and $\epsilon = 2.5 \pm 0.5 \text{ kJ/mol}$; for xenon $\sigma = 3.9 \pm 0.5 \text{ \AA}$ and $\epsilon = 3.9 \pm 0.8 \text{ kJ/mol}$.

4. Electronic-to-vibrational, -Rotational, and -Translational Energy Transfer:

S(¹D) + CO, N₂, O₂ and CO₂ Measured by Doppler Spectroscopy

Collisions of S(¹D) with CO, N₂, O₂ and CO₂ have been investigated to estimate the fraction of the sulfur electronic energy that is deposited in the internal degrees of freedom in the collision partner during the quenching of S(¹D) to S(³P). The experiment measures the Doppler profile of the S(³P) product, a profile that depends both on the amount of energy disposed into the internal degrees of freedom and on the differential scattering cross section for the inelastic collision. For CO and N₂ the results are consistent with a collision complex model for which the scattering is assumed to be isotropic in the collision plane and for which the energy is partitioned statistically into the degrees of freedom. Under the assumption of isotropic scattering, the results suggest that less energy than the statistical prediction is partitioned into translation for collisions with O₂, whereas more energy is partitioned into translation for CO₂.

5. Anisotropy and Energy Disposal in the 193-nm N₂O Photodissociation

Measured By VUV Laser-Induced Fluorescence of O(¹D)

Laser-induced fluorescence near 115 nm has been used to measure the Doppler profile of the O(¹D) product of 193-nm N₂O photolysis. The anisotropy of product recoil vectors is characterized by the parameter $\beta = 0.50 \pm 0.05$. The measured velocity distribution can be used to calculate a distribution of recoil energies that is in reasonable agreement with

that reported recently by Felder, Haas, and Huber; an average of 27.3 kcal/mole is deposited into translation, leaving ≈ 37 kcal/mole for the internal excitation of the N_2 fragment.

6. Photodissociation of OCS at 222 nm: The Triplet Channel

The dissociation of OCS at 222 nm produces both $S(^1D)$ and $S(^3P)$. By monitoring the Doppler profile of the minor $S(^3P_2)$ product on the $^3D_3^0 \leftarrow ^3P_2$ transition we have determined that the branching ratio for this triplet channel is 5% relative to the singlet channel. The Doppler profiles change as the angle between the polarization direction of the photolysis light and the propagation direction of the probe light is varied, indicating that the excited state lifetime of the OCS is short compared to its rotation period. Detailed analysis of the Doppler profiles provides an anisotropy parameter of $\beta = 0.3 \pm 0.2$ and a recoil speed distribution with an average of 37% of the $19,881 \text{ cm}^{-1}$ available energy. The remainder of the energy, $12,525 \text{ cm}^{-1}$, is deposited into CO vibration and rotation. The distributions for both the relative translation and the CO internal energy are broad.

B. Unpublished Projects

1. Photodissociation of O_3

The Hartley band photodissociation of ozone has been extensively investigated and is known to occur via two pathways; one yielding $O(^1D) + O_2(a^1\Delta_g)$ and the other $O(^3P) + O_2(X^3\Sigma_g^-)$. Studies indicate that the quantum yields for the excited singlet and ground state triplet product channels are .85 to .90 and .15 to .10, respectively. Recently, Turnipseed et al., examined the dissociation of ozone at 193 nm and determined that the quantum yield for excited state $O(^1D)$ atoms is $.46 \pm .29$. Molecular oxygen in the $b^1\Sigma_g^+$ state was also detected and quantified, $\Phi(b^1\Sigma) = .50 \pm .38$. It was therefore suggested that

$O(^1D)$ and $O_2(b^1\Sigma_g^-)$ are coproduced in the 193 nm photolysis of O_3 . We have measured the Doppler spectra of $O(^1D)$ products from the 248 and 193 nm photolysis of ozone in order to investigate further the transition from Hartley band dissociation channels and those observed in the vacuum ultraviolet. The $O(^1D)$ fragments produced were detected by laser-induced fluorescence via the one photon $2p^4(^1D_2)-3s^1(^1D^0_2)$ transition at 115.2 nm. Two-photon resonantly enhanced four-wave sum mixing in mercury yielded the required VUV radiation. The angular distributions and translational energy for the $O(^1D)$ atoms were deduced from the profiles. Present results indicate that ozone dissociation at 248 nm can be described by a parallel transition, whereas photolysis at 193 nm appears to result in an isotropic distribution of the velocity vectors with respect to the polarization direction of the dissociating light. It was also determined that $O(^1D)$ fragments produced in the 248 nm photolysis of O_3 have more energy in translation than the excited atomic oxygen fragments produced when O_3 is dissociated at 193 nm. These results and their implications concerning the existence of the $O(^1D) + O_2(b^1\Sigma_g^-)$ channel are still under analysis.